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(72) Inventors PAOLO DELLA PORTA and ELIO RABUSIN



(54) IMPROVEMENTS IN OR RELATING TO THE EVOLUTION OF ALKALI METAL VAPOURS IN VACUO

(71) We, S.A.E.S. GETTERS S.P.A., an Italian Company, of Via Gallarate, 215, Milan, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the evolution of alkali metal vapours in vacuo.

It is often desired to provide electronic tubes with an interior surface of an alkali metal or metals, such as caesium, potassium and/or sodium. Alkali metals are used, for example, in the formation of light-sensitive surfaces such as those of television camera tubes, photomultiplier tubes, electronic viewfinders, image-converter tubes and image intensifiers for radiological uses.

The alkali metal is conventionally introduced to tubes of the above kind by using dispensers which are adapted to release vapours of an alkali metal, inasmuch as they contain a compound of the desired alkali metal and a reducing agent therefor. Such a dispenser, employing silicon as the reducing agent for caesium chromate is disclosed in a paper by A. L. Eichenbaum and M. E. Moir "Caesium Vapour Dispenser" Rev. Sci. Instrum. 35. 691 (1964). Dispensers of this kind are also described in U.S. Patent Specification No. 2,117,735, in which a caesium chromate mixture is employed as the alkali metal source, together with a mixture of powdered zirconium and aluminium in the weight ratio of 8 to 1 as the reducing agent.

Unfortunately, mixtures adapted to set free vapours of an alkali metal according to the techniques outlined above and other conventional compositions evolve vapours of an alkali metal which are polluted by noxious gases,

such as oxygen. These gases react with the alkali metal and reduce the sensitivity to light of the resultant surface.

An object of the present invention is to provide a mixture which may be used to evolve vapours of an alkali metal with a considerable reduction in the abovementioned disadvantage. More particularly, it is an object of the present invention to provide mixtures which may be used to set free a substantially pure vapour of an alkali metal, substantially devoid of any noxious gases, such as oxygen.

According to the present invention a mixture adapted to evolve vapours of an alkali metal compound comprises as sole constituents an alkali metal compound and a zirconium-aluminium alloy as a reducing agent.

Mixtures have already been proposed which comprised a sintered matrix made of a sinterable material, such as iron, the matrix containing a chromate of an alkali metal and a zirconium-aluminium alloy as the chromate-reducing agent. However, it will be seen that such mixtures originate the evolution of undesirable gases, and it has been noted that such a gas-emission is due, more than anything, to the sintering operation and to exposure to air prior to installing the device in the interior of the final tube.

Zirconium-aluminium alloys having diversified grit sizes for their component particles have been used, as disclosed in the U.S. Patent Specification No. 3,385,644, in admixture with mercury oxide. These alloys, however, have never been used alone heretofore together with alkali metal compounds. In fact, it has been assumed that the alloy was incapable of catching the evolved gas with an adequate velocity, on account also of the necessity of operating

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with practically closed dispensers, so that any gas which possibly had escaped had only few chances of being recovered (differently from the mixtures of H_2O and Zr—Al alloys). It was also feared that loss of particles could occur when working without sinterable materials. An additional advantage of the mixture provided by the present invention lies in that there is no necessity of using the zirconium-aluminium alloy with a diversified grit size for the particles.

The alkali metal compound used in the mixtures according to this invention can be any compound capable of being reduced to its corresponding metal by a reducing agent and stable enough, both alone and in admixture with the reducing agent, as to withstand thermal treatments conventionally used for evacuating the vacuum-tubes. The preferred alkali metal compounds are those which are stable to temperatures up to $400^\circ C$, and which can be reduced when heated to temperatures in the range between $450^\circ C$ and $900^\circ C$. Examples of suitable alkali metal compounds are, among others, caesium chloride, sodium bichromate, and, preferably, caesium, potassium, sodium, rubidium and lithium chromates. Chromates are by far preferred to bichromates since they evolve less oxygen.

The reducing agents used in accordance with the invention are zirconium-aluminium alloys and, in general, those having a content of aluminium of from 5% to 30% on a weight basis, and preferably from 13% to 18% (the balance being zirconium) and especially those with the 16% by wt. of Al and 84% by wt. Zr, as produced with the method described in Italian Patent Specification No. 644,242. It is understood that the alloys may contain minor amounts of other impurities of a common nature and compatible metals, provided that they do not physically impair the properties of the mixture.

Both the alkali metal compounds and the Zr—Al alloy are preferably employed in the form of fine particles, generally of such a size as to pass through a sieve having 254 meshes per centimeter and, preferably 686 meshes per centimeter.

The alkali metal compound and the Zr—Al alloy can be blended in widely variable ratios, but, as a general rule, an excess of the Zr—Al alloy is used with respect to the stoichiometrical ratio so as completely to reduce the alkali metal compound. Generally, the weight ratio of the Zr—Al alloy to the reducible compound varies between 1:1 and 20:1, the range between 3:1 and 10:1 being preferred.

According to another aspect of the present invention a method is provided for the evolution of vapours of an alkali metal in a vacuum tube employing the mixture defined, including the steps of introducing to the tube a container which contains the mixture, sealing

the tube and connecting it to a vacuum pump, heating the tube to a temperature of between $300^\circ C$ and $400^\circ C$ during a time of from 1 to 8 hours whilst continually evacuating the tube of any residual gases, and finally heating the said mixture to a temperature in the range from $450^\circ C$ to $1000^\circ C$ to cause the evolution of alkali metal vapours.

The final heating step preferably takes place at between $550^\circ C$ and $900^\circ C$.

The invention will be further illustrated in the light of the following examples.

EXAMPLE 1.

This example illustrates the small amount of gas which is evolved when caesium chromate is reduced with a Zr—Al alloy. Five-hundred (500) grams of a Zr—Al alloy (16% by wt. Al; 84% by wt. Zr) were placed in a mortar and crushed with a pestle until a fine powder was obtained which passed through a screen having 686 meshes per centimeter; subsequently, the powder was blended with 100 grams of caesium chromate which had previously been crushed in the same manner. A portion of the blend was then introduced to a dispenser made of a Ni—Cr V alloy and having a slit. The dispenser was placed in a vacuum tube and the assembly heated for 8 hours at $375^\circ C$ in a vacuum of 10^{-8} Torr in order to remove the residual gases. The assembly was then allowed to cool and the dispenser alone was heated at $600^\circ C$, at this temperature the evaporation of caesium begins to occur. The temperature was then gradually increased at a rate of $8^\circ C$ per minute until attaining a maximum value of $850^\circ C$ this temperature being maintained for one minute. The caesium vapour was deposited on the cold walls of the tube: the latter during evolution of the caesium vapours, being connected to a vacuum pump through a duct having a throttled section which acted as a calibrated orifice for reducing the gas rate of flow. The pressures at both sides of the orifice were continually recorded during progress of the evolution of the caesium vapours, and the overall amount of evolved gases was calculated with the following formula:

$$Q = C \int_{t_0}^{t_1} [P_D(t) - P_P(t)] dt$$

where;

Q is the amount of gas, in cu.cms. Torr

C is the rate of flow of the orifice (146 cu.cms/sec)

P_D is the pressure upstream of the throttled section, in Torr

P_P is the pressure obtaining downstream of throttled section, in Torr

t_0 is the instant of time at which the evolution of caesium vapours is started, in seconds

t_1 is the instant of time at which the evolution

of caesium vapours is completed, in seconds, and
dt is the time differential.

- 5 It was found that 0.3 cu.cms. Torr of gas per milligram of caesium chromate had been evolved.

EXAMPLE 2.

10 This comparative example is illustrative of the considerable amount of gas evolved chromate when reduced with a mixture of one part by weight of aluminium and 8 parts by weight of zirconium, according to the method of U.S. Patent Specification No. 2,117,735.

15 The procedure of Example 1 was repeated by employing the same times, temperatures, working conditions and ingredients, with the only exception that the Zr—Al alloy was replaced by an equivalent weight of a blend of 1 part by weight of Al and 8 parts by weight of Zr.

20 12 Cu.cms. Torr of evolved gas per milligram of caesium chromate were detected, that is approximately 40 times the amount of gas evolved in Example 1, in which the Zr—Al alloy was employed as the reducing agent.

EXAMPLE 3.

30 This comparative example shows the increase of the amount of gas evolved during the reduction of caesium chromate from a blend consisting of 1 part by weight caesium chromate, 4 parts by weight of Zr—Al alloy (84% by wt. Zr plus 16% by wt. of Al) and 3 parts by weight of Fe.

35 The individual components of the blend were prepared as described in Example 1 and then blended together, and a portion of the blend was placed in a slitted container.

40 By heating the blend-containing vessel in a vacuum at 450°C to obtain iron sintering and then exposing the dispenser to air prior to installing it in the interior of a vacuum tube and following the same procedure as described in Example 1, it has been ascer-
45 tained that the amount of gas evolved was 3.5 cu.cm. Torr per milligram of caesium chromate, that is approximately 12 times the amount of gas evolved in Example 1.

EXAMPLE 4.

50 The procedure of Example 1 was repeated twice with the same times, temperatures, ingredients and working conditions, the first time with the exception that caesium chromate was substituted by an equal amount by weight of sodium chromate, and the second time with the exception that caesium chromate was replaced by an equal amount by weight of potassium chromate. Similar results were obtained in the two cases, the amounts of gas evolved together with the sodium (or potas-
55 sium, respectively) vapours being small.

The term "cu.cms.Torr" as used in the examples, refers to the volume of the gas in cubic centimeters at the pressure of 1 Torr (1 mmHg.absol.) and is the measure of an amount of gas irrespective of the pressure at which the operation is carried out. 65

By comparing Examples 1 and 2 it is easy to appreciate that the composition according to the U.S. Patent Specification No. 2,117,735 cited above evolves an amount of noxious gases which is 40 times as great as the one evolved by the composition according to the present invention. 70

A comparison between Example 1 and Example 3 shows that the sintering operation of the sinterable material which is present causes a considerable increase of the amount of gas evolved during the evolution of the alkali metal vapours with respect to the amount evolved by the composition according to the present invention. 75 80

WHAT WE CLAIM IS:—

1. A mixture adapted to evolve vapours of an alkali metal, comprising as sole constituents an alkali metal compound, and a zirconium-aluminum alloy as a reducing agent. 85

2. A mixture as claimed in claim 1, in which the metal compound is an alkali metal chromate.

3. A mixture as claimed in either claim 1 or claim 2, in which the Zr—Al alloy is present in excess with respect to the stoichiometrically calculated amount for its action as a reducing agent. 90

4. A mixture as claimed in claim 3, in which the Zr—Al alloy is present in a weight ratio of from 3:1 to 10:1 with respect to the alkali metal compound. 95

5. A mixture as claimed in any one of claims 1 to 4, in which the alloy and the alkali metal compound are both finely divided and have such a grit size as to pass through a screen of at least 254 meshes per centimetre. 100

6. A mixture as claimed in any one of the preceding claims, in which the Zr—Al alloy contains from 5 to 30 parts by weight of aluminium, the balance being zirconium. 105

7. A mixture as claimed in claim 6, in which the Zr—Al alloy contains 13 to 18 parts by weight of aluminium the balance being zirconium. 110

8. A mixture as claimed in claim 7, in which the alloy comprises 16 parts of Al and 84 parts of Zr, on a weight basis. 115

9. A method for setting free vapours of an alkali metal in a vacuum tube by employing a mixture as claimed in any one of the preceding claims, including the steps of introducing to the tube a container which contains the mixture, sealing the tube and connecting it to a vacuum pump, heating the tube to a temperature of between 300°C and 400°C during a time of from 1 to 8 hours 120

- whilst continually evacuating the tube of any residual gases, and finally heating the said mixture to a temperature in the range from 350°C to 1000°C to cause the evolution of alkali metal vapours.
- 5 10. A mixture adapted to evolve vapours of an alkali metal substantially as described herein with reference to Examples 1 and 4.
11. A method for setting free vapours of an alkali metal within a vacuum tube substantially as described with reference to Examples 1 and 4. 10

ABEL & IMRAY,
Chartered Patent Agents,
Quality House, Quality Court, Chancery Lane,
London, W.C.2.

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